

WHAT IS CLAIMED IS:

1. A pattern forming method comprising:  
forming a photosensitive resin film on a  
substrate;  
5 exposing the photosensitive resin film;  
forming a pattern of the photosensitive resin film  
by supplying a developing solution to the  
photosensitive resin film; and  
slimming to remove a surface layer of the pattern  
10 by causing the pattern to contact with an activated  
water.
2. The pattern forming method according to  
claim 1, wherein supercritical water or subcritical  
water is used as the activated water.
- 15 3. The pattern forming method according to  
claim 1, wherein the activated water contains radicals  
of atoms or molecules produced by irradiating the water  
with light.
- 20 4. The pattern forming method according to  
claim 3, wherein the light includes wavelength of  
250 nm or less.
5. The pattern forming method according to  
claim 1, wherein the activated water contains radicals  
produced by irradiating the water in which molecules of  
25 gas are dissolved, with light.
6. The pattern forming method according to  
claim 5, wherein, when hydrogen peroxide is selected as

the molecules of gas, the light includes wavelength of 300 nm or less.

7. The pattern forming method according to claim 5, wherein, when oxygen or ozone is selected as the molecules of gas, the light includes wavelength of 250 nm or less.

8. The pattern forming method according to claim 1, wherein the activated water is ozone water which ozone dissolved in pure water, and the pattern surface is oxidized by 5 nm or more with the ozone water.

9. The pattern forming method according to claim 1, wherein the pattern dimension is measured before the slimming process, and the condition of the slimming process is determined on the basis of the result of measurement.

10. The pattern forming method according to claim 9, wherein the pattern dimension is measured by emitting a measuring light to a measuring region of the substrate, and determining on the basis of any one of the diffracted light intensity from the measuring region, wavelength dispersion of the diffracted light intensity, and wavelength dispersion of polarized light information of the diffracted light.

11. The pattern forming method according to claim 1, wherein the slimming process is followed by one or more repetitions of a re-slimming process of

removing a surface layer of the pattern by causing the pattern to contact with the activated water.

12. The pattern forming method according to claim 11, wherein the pattern dimension is measured  
5 before the re-slimming process.

13. The pattern forming method according to claim 12, wherein the pattern dimension is measured by emitting a measuring light to a measuring region of the substrate, and determining on the basis of any one of  
10 the diffracted light intensity from the measuring region, wavelength dispersion of the diffracted light intensity, and wavelength dispersion of polarized light information of the diffracted light.

14. The pattern forming method according to claim 13, wherein the condition of the re-slimming  
15 process is determined on the basis of the result of measurement of the measured pattern dimension.

15. The pattern forming method according to claim 13, wherein the re-slimming process is stopped at  
20 the time when the measured pattern dimension reaches a desired dimension.

16. The pattern forming method according to claim 1, wherein the pattern dimension is measured along with the slimming process, and the slimming  
25 process is stopped at the time when the measured pattern dimension reaches a desired dimension.

17. The pattern forming method according to

claim 1, wherein, after forming the pattern, a cleaning  
solution is supplied on the substrate in which the  
developing solution is supplied, and the slimming  
process is executed while the cleaning solution is left  
5 over on the substrate.

18. The pattern forming method according to  
claim 1, wherein, after forming the pattern, a cleaning  
solution is supplied on the substrate in which the  
developing solution is supplied, and the slimming  
10 process is executed after the cleaning solution is  
removed from the substrate.

19. The pattern forming method according to  
claim 1, further comprising, after the slimming  
process:

15 supplying carbon dioxide in a supercritical state  
on the substrate to dissolve the water on the  
substrate; and

drying the substrate while varying the pressure  
and temperature such that the carbon dioxide in the  
20 supercritical state is transformed into a gaseous state  
without transition of a liquid state.

20. The pattern forming method according to  
claim 1, further comprising, after the slimming  
process:

25 transforming the water into a supercritical state  
while varying the pressure and temperature such that  
the activated water is not vaporized; and

drying the substrate while varying the pressure and temperature such that the water in the supercritical state is transformed into a gaseous state without transition of a liquid state.

5           21. A pattern forming method comprising:

          forming a photosensitive resin film on a substrate;

          exposing the photosensitive resin film;

          reforming a surface layer of the pattern by

10       causing the pattern to contact with an activated water;  
          and

          removing the surface layer of the pattern by  
          supplying a developing solution to the pattern.

          22. The pattern forming method according to  
15       claim 21, wherein supercritical water or subcritical  
          water is used as the activated water.

          23. The pattern forming method according to  
          claim 21, wherein the activated water contains radicals  
          of atoms or molecules produced by irradiating the water  
20       with light.

          24. The pattern forming method according to  
          claim 23, wherein the light includes wavelength of  
          250 nm or less.

          25. The pattern forming method according to  
25       claim 21, wherein the activated water contains radicals  
          produced by irradiating the water in which molecules of  
          gas are dissolved, with light.

26. The pattern forming method according to claim 25, wherein, when hydrogen peroxide is selected as the molecules of gas, the light includes wavelength of 300 nm or less.

5        27. The pattern forming method according to claim 25, wherein, when oxygen or ozone is selected as the molecules of gas, the light includes wavelength of 250 nm or less.

10       28. The pattern forming method according to claim 21, wherein the activated water is ozone water having ozone dissolved in pure water, and the pattern surface is oxidized by 5 nm or more with the ozone water.

15       29. The pattern forming method according to claim 21, wherein the process of removing the surface layer of the pattern is followed by one or more repetitions of re-reforming process of reforming the surface layer of the pattern by causing the pattern to contact with the activated water, and a re-developing process of removing the surface layer of the pattern by  
20       supplying a developing solution to the re-reformed pattern.

25       30. The pattern forming method according to claim 29, wherein the pattern dimension is measured before the re-reforming process.

31. The pattern forming method according to claim 30, wherein the condition of the re-reforming

process and re-developing process is determined on the basis of the measured pattern dimension.

32. The pattern forming method according to claim 30, wherein the pattern dimension is measured by emitting a measuring light to a measuring region of the substrate, and determining on the basis of any one of the diffracted light intensity from the measuring region, wavelength dispersion of the diffracted light intensity, and wavelength dispersion of polarized light information of the diffracted light.

33. A pattern forming method comprising:  
forming a photosensitive resin film on a substrate;  
exposing the photosensitive resin film;  
reforming a surface layer of the photosensitive resin film by causing the photosensitive resin film to contact with an activated water; and  
forming a pattern of the photosensitive resin film by supplying a developing solution to the photosensitive resin film of which surface layer has been reformed.

34. The pattern forming method according to claim 33, wherein supercritical water or subcritical water is used as the activated water.

35. The pattern forming method according to claim 33, wherein the activated water contains radicals of atoms or molecules produced by irradiating the water

with light.

36. The pattern forming method according to claim 35, wherein the light includes wavelength of 250 nm or less.

5        37. The pattern forming method according to claim 33, wherein the activated water contains radicals produced by irradiating the water in which molecules of gas are dissolved, with light.

10       38. The pattern forming method according to claim 37, wherein, when hydrogen peroxide is selected as the molecules of gas, the light includes wavelength of 300 nm or less.

15       39. The pattern forming method according to claim 37, wherein, when oxygen or ozone is selected as the molecules of gas, the light includes wavelength of 250 nm or less.

20       40. The pattern forming method according to claim 33, wherein the activated water is ozone water having ozone dissolved in pure water, and the pattern surface is oxidized by 5 nm or more with the ozone water.

41. A pattern forming method comprising:

forming a photosensitive resin film on a substrate;

25       exposing the photosensitive resin film;

reforming a surface layer of the photosensitive resin film by causing the photosensitive resin film to



contact with an activated water; and

forming a pattern of the photosensitive resin film  
by supplying a developing solution to the photo-  
sensitive resin film of which surface layer has been  
5 reformed.

42. The pattern forming method according to  
claim 41, wherein supercritical water or subcritical  
water is used as the activated water.

43. The pattern forming method according to  
10 claim 41, wherein the activated water contains radicals  
of atoms or molecules produced by irradiating the water  
with light.

44. The pattern forming method according to  
claim 43, wherein the light includes wavelength of  
15 250 nm or less.

45. The pattern forming method according to  
claim 33, wherein the activated water contains radicals  
produced by irradiating the water in which molecules of  
gas are dissolved, with light.

20 46. The pattern forming method according to  
claim 45, wherein, when hydrogen peroxide is selected  
as the molecules of gas, the light includes wavelength  
of 300 nm or less.

25 47. The pattern forming method according to  
claim 45, wherein when oxygen or ozone is selected as  
the molecules of gas, the light includes wavelength of  
250 nm or less.

48. The pattern forming method according to claim 41, wherein the activated water is ozone water having ozone dissolved in pure water, and the pattern surface is oxidized by 5 nm or more with the ozone  
5 water.

49. A substrate processing apparatus comprising:  
a substrate holding mechanism which holds a substrate almost horizontally;  
a light emitting section including a transparent  
10 plate disposed oppositely to the substrate holding mechanism, the light emitting section emitting light to the substrate through the transparent plate; and  
a distance adjusting mechanism which adjusts the distance between the light emitting section and the  
15 substrate such that, when a liquid film is formed on the substrate, the transparent plate contacts with the liquid film.

50. The substrate processing apparatus according to claim 49, further comprising a moving mechanism  
20 which relatively moves the light emitting section and the substrate holding mechanism horizontally.

51. The substrate processing apparatus according to claim 49, wherein the substrate holding mechanism is substantially same as the substrate in diameter.

25 52. The substrate processing apparatus according to claim 49, further comprising a rotating mechanism which rotates the substrate held in the substrate

holding mechanism.

53. The substrate processing apparatus according to claim 49, wherein the distance adjusting mechanism adjusts the distance between the top of the substrate and the transparent plate such that the transmissivity of the illuminating light to the liquid between the transparent plate and the substrate is 1% or more.

54. The substrate processing apparatus according to claim 49, further comprising a measuring mechanism which measures the distance between the substrate and the light emitting section, wherein the distance adjusting mechanism adjusts the distance on the basis of the result measured by the measuring mechanism.

55. The substrate processing apparatus according to claim 49, further comprising an illumination detecting mechanism which detects the illumination of the light emitted from the light emitting section.

56. The substrate processing apparatus according to claim 55, wherein, when the detected illumination is larger than a reference value, the distance adjusting mechanism sets the distance between the substrate and the light emitting section longer than the distance corresponding to the reference value.

57. The substrate processing apparatus according to claim 55, wherein, when the detected illumination is smaller than a reference value, the distance adjusting mechanism sets the distance between the substrate and

the light emitting section shorter than the distance corresponding to the reference value.

58. The substrate processing apparatus according to claim 50, further comprising an illumination  
5 detecting mechanism which detects the illumination of the light emitted from the light emitting section, wherein, when the detected illumination is larger than a reference value, the moving mechanism sets the relative moving speed of the light emitting section and  
10 the substrate holding mechanism faster than the moving speed corresponding to the reference value.

59. The substrate processing apparatus according to claim 50, further comprising an illumination  
15 detecting mechanism which detects the illumination of the light emitted from the light emitting section, wherein, when the detected illumination is smaller than a reference value, the moving mechanism sets the relative moving speed of the light emitting section and the substrate holding mechanism slower than the moving  
20 speed corresponding to the reference value.

60. The substrate processing apparatus according to claim 49, further comprising a liquid supply device which supplies the liquid onto the substrate to form a film of the liquid.

25 61. The substrate processing apparatus according to claim 50, further comprising a liquid supply device which supplies the liquid onto the substrate to form a

film of the liquid, and a liquid suction device which sucks the liquid on the substrate.

62. The substrate processing apparatus according to claim 60, wherein the distance adjusting mechanism  
5 adjusts the interval between the top of the substrate and the transparent plate at 0.5 mm or less.

63. The substrate processing apparatus according to claim 60, wherein the moving mechanism relatively moves the light emitting section and the liquid supply  
10 device, and the substrate holding mechanism horizontally.

64. The substrate processing apparatus according to claim 63, wherein the liquid supply device and the light emitting section are disposed in this order from  
15 the front side in the moving direction of the light emitting section and the liquid supply device with respect to the substrate holding mechanism.

65. The substrate processing apparatus according to claim 61, wherein the moving mechanism relatively  
20 moves the light emitting section, liquid supply device, and liquid suction device, and the substrate holding mechanism horizontally.

66. The substrate processing apparatus according to claim 65, wherein the liquid supply device, the  
25 light emitting section, and the liquid supply device are disposed in this order from the front side in the moving direction of the light emitting section, liquid

supply device, and liquid suction device with respect to the substrate holding mechanism.

67. The substrate processing apparatus according to claim 49, wherein the light emitting section  
5 comprises a plurality of light sources, and an illumination adjusting mechanism which adjusts the illumination of each light source.

68. The substrate processing apparatus according to claim 49, wherein the light emitting section  
10 distributes the light from the light sources and emits to a plurality of regions on the substrate.

69. The substrate processing apparatus according to claim 50, wherein the width of the illumination region of the light emitting section in a direction  
15 orthogonal to the horizontal moving direction is substantially same as the diameter of the substrate.

70. The substrate processing apparatus according to claim 49, further comprising a developing solution supply device which supplies a developing solution to  
20 the substrate.

71. A substrate processing apparatus comprising:  
a substrate holding mechanism which holds a substrate almost horizontally;  
a liquid supply section which supplies a liquid  
25 onto the substrate;  
a light emitting section which emits light to the liquid before being supplied on the substrate; and

a moving mechanism which moves relatively the liquid supply section and light emitting section, and the substrate holding mechanism horizontally.

72. The substrate processing apparatus according to claim 71, further comprising a distance adjusting mechanism which adjusts the distance between the liquid supply section and the substrate.

73. The substrate processing apparatus according to claim 72, further comprising a measuring mechanism which measures the distance between the substrate and the liquid supply section, wherein the distance adjusting mechanism adjusts the distance on the basis of the result measured by the measuring mechanism.

74. The substrate processing apparatus according to claim 71, wherein the substrate holding mechanism is substantially same as the substrate in diameter.

75. The substrate processing apparatus according to claim 71, further comprising a rotating mechanism which rotates the substrate held by the substrate holding mechanism.

76. The substrate processing apparatus according to claim 71, further comprising an illumination detecting mechanism which detects the illumination of the light emitted from the light emitting section.

77. The substrate processing apparatus according to claim 76, wherein, when the detected illumination is larger than a reference value, the distance adjusting

mechanism sets the distance between the substrate and the light emitting section longer than the distance corresponding to the reference value.

5       78. The substrate processing apparatus according to claim 76, wherein, when the detected illumination is smaller than a reference value, the distance adjusting mechanism sets the distance between the substrate and the light emitting section shorter than the distance corresponding to the reference value.

10       79. The substrate processing apparatus according to claim 71, further comprising an illumination detecting mechanism which detects the illumination of the light emitted from the light emitting section, wherein, when the detected illumination is larger than  
15       a reference value, the moving mechanism sets the relative moving speed of the light emitting section and the substrate holding mechanism faster than the moving speed corresponding to the reference value.

20       80. The substrate processing apparatus according to claim 71, further comprising an illumination detecting mechanism which detects the illumination of the light emitted from the light emitting section, wherein, when the detected illumination is smaller than  
25       a reference value, the moving mechanism sets the relative moving speed of the light emitting section and the substrate holding mechanism slower than the moving speed corresponding to the reference value.



81. The substrate processing apparatus according to claim 71, wherein the light emitting section comprises a plurality of light sources, and an illumination adjusting mechanism which adjusts the illumination of each light source.

82. The substrate processing apparatus according to claim 71, wherein the light emitting section distributes the light from the light sources and emits to a plurality of regions on the substrate.

83. The substrate processing apparatus according to claim 71, wherein the width of the illumination region of the light emitting section in a direction orthogonal to the horizontal moving direction is substantially same as the diameter of the substrate.

84. The substrate processing apparatus according to claim 71, further comprising a developing solution supply device which supplies a developing solution to the substrate.

85. A method of manufacturing a semiconductor device, comprising:

forming a resin film on the principal plane of a substrate to be processed;

causing the principal plane of the substrate to be processed to contact with an atmosphere containing molecules to produce OH radicals and/or O radicals when irradiated with an ultraviolet light;

emitting the ultraviolet light to the principal

plane of the substrate to be processed;

producing OH radicals and/or O radicals from the molecules by the ultraviolet light;

producing a reaction product by reaction between  
5 the produced OH radicals and/or O radicals and the resin film; and

cooling the substrate to be processed to a temperature at which the resultant reaction product is not fluidized at the time of illumination with the  
10 ultraviolet ray.

86. The method according to claim 85, wherein the resin film is formed in a predetermined pattern.

87. The method according to claim 86, further comprising removing the reaction product from the  
15 principal plane of the substrate to be processed.

88. The method according to claim 85, wherein the molecules are one or more selected from oxygen and ozone.

89. The method according to claim 87, wherein the  
20 substrate to be processed is etched by using the resin film as a mask after removing the reaction product.

90. The method according to claim 87, wherein the principal plane of the substrate to be processed is irradiated with ultraviolet light or electron beam  
25 after removing the reaction product.

91. The method according to claim 87, wherein removing of the reaction product includes supplying a

solution for dissolving the reaction product to the principal plane of the substrate to be processed, and removing the solution from the principal plane of the substrate to be processed.

5           92. The method according to claim 91, wherein the solution is water or hydrogen peroxide.

93. The method according to claim 91, further comprising, after removing the solution, drying the principal plane of the substrate to be processed.

10           94. The method according to claim 87, wherein the reaction product is removed by heating the substrate to be processed to a temperature at which the reaction product is vaporized.

15           95. The method according to claim 94, wherein the heating temperature of the substrate to be processed is less than the pyrolysis temperature of the resin film.

20           96. The method according to claim 87, wherein a series of process of contact with the atmosphere, generation of the OH radicals and/or O radicals, generation of the reaction product, and removal of the reaction product is executed plural times.

25           97. The method according to claim 85, wherein the molecules are liquid in a vapor state, and the liquid is adsorbed on the surface of the resin film by contact with the atmosphere.

98. The method according to claim 97, further comprising increasing the contact angle of the surface

of the resin film to the liquid.

99. The method according to claim 97, wherein the liquid is water or hydrogen peroxide.

100. The method according to claim 85, wherein  
5 contact with the atmosphere is executed with the principal plane of the substrate to be processed directed downward.

101. A method of manufacturing a semiconductor device, comprising:

10 forming a pattern of a resin film on the principal plane of a substrate to be processed;

directing the principal plane of the substrate to be processed in a downward direction;

causing the principal plane of the substrate to be  
15 processed to contact with an atmosphere containing molecules to produce OH radicals and/or O radicals when irradiated with an ultraviolet light;

emitting the ultraviolet light to the principal plane of the substrate to be processed;

20 producing OH radicals and/or O radicals from the molecules by the ultraviolet light;

producing a reaction product by reaction between the produced OH radicals and/or O radicals and the resin film; and

25 removing the reaction product.

102. The method according to claim 101, wherein the reaction product is fluidized at the time of emitting

the ultraviolet light.

103. The method according to claim 101, wherein the molecules are one or more selected from oxygen and ozone.

5        104. The method according to claim 101, wherein the substrate to be processed is etched by using the resin film as a mask after removing the reaction product.

105. The method according to claim 101, wherein the principal plane of the substrate to be processed is  
10 irradiated with ultraviolet light or electron beam after removing the reaction product.

106. The method according to claim 101, wherein removing of the reaction product includes supplying a solution for dissolving the reaction product to the  
15 principal plane of the substrate to be processed, and removing the solution from the principal plane of the substrate to be processed.

107. The method according to claim 106, wherein the solution is water or hydrogen peroxide.

20        108. The method according to claim 106, further comprising, after removing the solution, drying the principal plane of the substrate to be processed.

109. The method according to claim 101, wherein the reaction product is removed by heating the substrate to  
25 be processed to a temperature at which the reaction product is vaporized.

110. The method according to claim 109, wherein the

heating temperature of the substrate to be processed is less than the pyrolysis temperature of the resin film.

111. The method according to claim 101, wherein a series of process of contact with the atmosphere,  
5 generation of the OH radicals and/or O radicals, generation of the reaction product, and removal of the reaction product is executed plural times.

112. The method according to claim 101, wherein the molecules are liquid in a vapor state, and the liquid  
10 is adsorbed on the surface of the resin film by contact with the atmosphere.

113. The method according to claim 112, further comprising increasing the contact angle of the surface of the resin film to the liquid.

15 114. The method according to claim 112, wherein the liquid is water or hydrogen peroxide.

115. A substrate processing method comprising:

forming a pattern of a resin film on the principal plane of a substrate to be processed;

20 causing the principal plane of the substrate to be processed to contact with an atmosphere containing molecules to produce OH radicals and/or O radicals when irradiated with an ultraviolet light;

emitting the ultraviolet light to the principal  
25 plane of the substrate to be processed;

producing OH radicals and/or O radicals from the molecules by the ultraviolet light;

producing a reaction product by reaction between the produced OH radicals and/or O radicals and the resin film;

5 heating the substrate to be processed so as to evaporate the reaction product at a temperature of the resin film less than the decomposition temperature when irradiated with the ultraviolet light; and

removing the reaction product after irradiation with the ultraviolet light.

10 116. The method according to claim 115, wherein the substrate to be processed is set at a pressure of less than the atmospheric pressure when heating the substrate to be processed.

15 117. The method according to claim 115, wherein the molecules are one or more selected from oxygen and ozone.

118. The method according to claim 115, wherein the substrate to be processed is etched by using the resin film as a mask after removing the reaction product.

20 119. The method according to claim 115, wherein the principal plane of the substrate to be processed is irradiated with ultraviolet light or electron beam after removing the reaction product.

25 120. The method according to claim 115, wherein the removal of the reaction product includes supplying a solution for dissolving the reaction product to the principal plane of the substrate to be processed, and

removing the solution from the principal plane of the substrate to be processed.

121. The method according to claim 120, wherein the solution is water or hydrogen peroxide.

5        122. The method according to claim 120, wherein the removal of the solution is followed by drying the principal plane of the substrate to be processed.

123. The method according to claim 115, wherein the reaction product is removed by heating the substrate to  
10 be processed to a temperature at which the reaction product is vaporized.

124. The method according to claim 123, wherein the heating temperature of the substrate to be processed is less than the pyrolysis temperature of the resin film.

15        125. The method according to claim 115, wherein contact with the atmosphere is executed with the principal plane of the substrate to be processed directed downward.

126. A substrate processing apparatus comprising:  
20        a chamber;

substrate holding means provided in the chamber,  
for holding a substrate;

means for controlling the temperature of the substrate;

25        means for emitting an ultraviolet light, disposed opposite to the principal plane of the substrate held by the substrate holding means;



gas supply means connected to the chamber, in a space between the substrate principal plane and the emitting means, for supplying a gas containing molecules to produce OH radicals and/or O radicals  
5 by irradiation with the ultraviolet ray into the chamber;

gas exhaust means for exhausting the chamber; and  
concentration control means for controlling the concentration of the molecules contained in the gas  
10 that is supplied from the gas supply means.

127. The substrate processing apparatus according to claim 126, wherein the substrate holding means holds the substrate with its principal plane directed downward.

15 128. The substrate processing apparatus according to claim 126, further comprising means for scanning the light emitting means relatively to the substrate.

129. The substrate processing apparatus according to claim 126, wherein the gas supply means has a  
20 bubbler filled with a liquid containing molecules.

130. The substrate processing apparatus according to claim 126, further comprising cleaning means for cleaning the principal plane of the substrate by supplying a liquid to the principal plane of the  
25 substrate.

131. The substrate processing apparatus according to claim 130, further comprising drying means for

drying the liquid remaining on the principal plane of the substrate.